

## Experiment 28: Qualitative Analysis of Cations

(This experiment was adapted from Colby College, Experiment 4.)

### Purpose

The purpose of this experiment is to develop and use an chemical-test analysis scheme (flow chart) for the identification of cations.

### Background *(This is a fictional story.)*

Chemical Solutions Incorporated (CSI) has earned a contract from the City of Trenton, which is trying to identify the source of metal contamination detected in the Delaware River. Excessively high levels of the heavy metal cations  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ba}^{2+}$  have been detected in the region of the Trenton State House, which has concerned legislators thinking about the possible impact of the contamination on tourism in the area. The businesses that are likely suspects for contributing one or more heavy metal cations to the river water (Figure 1) are: Smiley's Photo Studio (1), Callie's Computer Chips (2), Central NJ Testing (3), Peaceful Valley Funeral Home (4), Axel's Auto Body & Repair (5), Evergreen Paper Mill (6), Monet's Art Restoration (7), Stay Dry Cleaners (8), and Call of the Wild Taxidermy (9).

CSI's research team has compiled a useful summary below on inorganic qualitative analysis, which can be used to detect ions present in a water sample. We will use these methods to separate and identify the presence (or absence) of the relevant cations in river water samples collected near each of the suspect facilities that have been provided by the City of Trenton. Additionally, the City would like an easy to follow, effective qualitative analysis scheme that they can use to monitor the river water for these cations from now on.

Therefore, every CSI investigator (you are an investigator) will develop a qualitative analysis scheme to separate each cation and confirm its identity. This scheme will be used to test water samples taken from two of the nine possible pollution sites. For the separation and detection of the cations in question, you will use reactions that involve different tendencies of these ions to precipitate, form complex ions, or display amphoteric behavior. To familiarize yourself with these different chemical properties, you will first do standard tests to observe the characteristic behavior of each cation before testing the river samples.

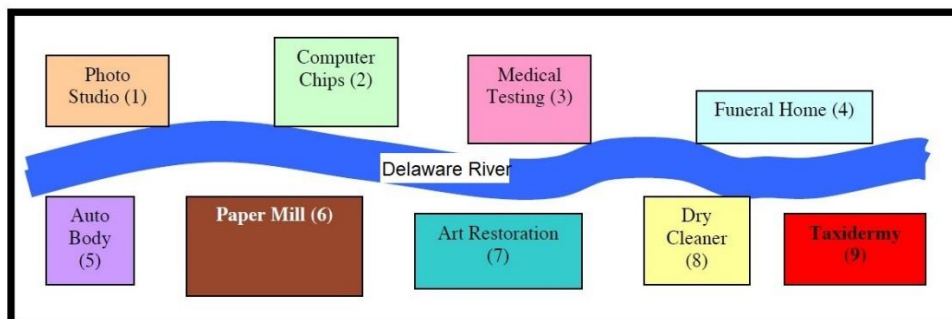


Figure 1. Map of the contaminated area of the Delaware River with possible rogue polluters.

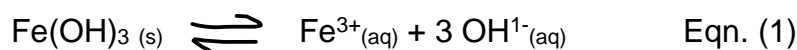
## Qualitative Analysis Summary

### I. Sparingly Soluble Salts

Some cations form relatively insoluble salts that precipitate out of aqueous solution. For example, chloride salts are generally soluble with the notable exceptions of the salts containing  $\text{Ag}^+$ ,  $\text{Pb}^{+2}$ , and  $\text{Hg}_2^{2+}$ . Similarly, most sulfate salts are soluble except  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{Hg}_2\text{SO}_4$ ,  $\text{AgSO}_4$ , and  $\text{CaSO}_4$ .

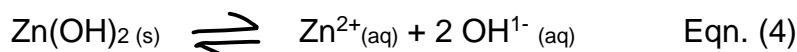
**Therefore, the addition of  $\text{Cl}^{1-}$  can be used to test for silver(I) cations and the addition of  $\text{SO}_4^{2-}$  can be used to test for the silver(I) and barium cations.**

Most hydroxide salts are insoluble. For example, the solubility of  $\text{Fe}^{3+}$  in basic solution is governed by the reaction shown in Eqn. 1, from which the corresponding equilibrium constant expression can be derived (Eqn. 2). The equilibrium constant for the reaction  $K_{\text{sp}}$  is  $6.3 \times 10^{-38}$ , which says that  $\text{Fe}(\text{OH})_3$  is sparingly soluble under most conditions. Indeed, for hydroxide concentrations greater than  $10^{-11}$  M ( $\text{pH} > 3$ ),  $\text{Fe}^{3+}$  is relatively insoluble. Therefore, in a qualitative analysis scheme,  $\text{Fe}^{3+}$  may be removed from solution by making the solution basic, thereby precipitating  $\text{Fe}(\text{OH})_3$ . This precipitate can be removed from solution by centrifugation.



$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^{1-}]^3 \quad \text{Eqn. (2)}$$

However, other cations for which you are testing also form insoluble hydroxides. Therefore, the addition of base to a mixture of cations may precipitate other metal hydroxides in addition to  $\text{Fe}(\text{OH})_3$ . For example, if  $\text{Zn}^{2+}$  is also present, the analogous reaction and relationships hold (eqns. 4-5). Copper also forms a hydroxide precipitate.



$$K_{\text{sp}} = [\text{Zn}^{2+}][\text{OH}^{1-}]^2 = 4.5 \times 10^{-17} \quad \text{Eqn. (5)}$$

At hydroxide concentrations greater than  $10^{-6}$  M ( $\text{pH} > 8$ ),  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  are insoluble and would coprecipitate as their hydroxides. In theory, one might be able to adjust the pH to the range where  $\text{Fe}^{3+}$  will precipitate but  $\text{Zn}^{2+}$  will not, but in practice this approach works poorly. Alternative approaches to separating  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  are either to use the amphoteric nature of  $\text{Zn}(\text{OH})_2$  or the ability of  $\text{Zn}^{2+}$  to form complex ions as described below.

**Therefore, the addition of  $\text{OH}^{1-}$  can be used to form precipitates of copper(II), iron(III), silver(I), and zinc(II).**

### II. Amphoteric Hydroxides

Some metal-hydroxide precipitates dissolve in excess hydroxide solutions because of the formation of soluble hydroxide complex ions, as seen for  $\text{Zn}^{2+}$  in eqn. 7. Such hydroxides are called amphoteric hydroxides because they will react with and dissolve

in both acid and base. The equilibrium constant for this reaction is very product-favored ( $K = 2 \times 10^{20}$ ). Therefore,  $\text{Zn(OH)}_2$  solid will form when small amounts of a strong base are added to a  $\text{Zn}^{2+}$  containing solution, but the continued addition of strong base will dissolve that precipitate as  $[\text{Zn(OH)}_4]^{2-}$  is formed. This amphoteric behavior is useful in qualitative analysis.



**Therefore, the addition of excess  $\text{OH}^{1-}$  can be used to separate the zinc(II) cation from the copper(II), iron(III), and silver(I) cations.**

### III. Complex Ion Formation

The formation of other complexes ions can also be useful. For example,  $\text{Cu}^{2+}$  and ammonia react to form the complex ion  $[\text{Cu(NH}_3)_4]^{2+}$  (eq 8) with a large equilibrium constant ( $K = 4.8 \times 10^{12}$ ), showing that the formation of  $[\text{Cu(NH}_3)_4]^{2+}$  is very favorable. The utility of ammonia in qualitative analysis schemes can be shown by the behavior of a mixture of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions. If concentrated ammonia (a basic solution because ammonia is a weak base, eqn. (9)) is added to a solution containing  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions,  $\text{Fe(OH)}_3$  will precipitate in the presence of base (eqn. 1) and the soluble complex ion  $[\text{Cu(NH}_3)_4]^{2+}$  will remain in solution, separating the  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions.



**Therefore the addition of  $\text{NH}_3$  can be used to separate the Cu(II) cation from the iron(III), silver(I), and zinc(II) cations.**

### V. The Presence of Colored Ions

A preliminary examination of an unknown that may contain a colored cation can yield valuable information. Two of the cations for which you are testing are colored:  $\text{Fe}^{3+}$  (rust or yellow), and  $\text{Cu}^{2+}$  (aqua). If the solution is colorless, you know immediately that these two ions are either absent or present in extremely low concentrations. However, in your role as a highly paid consultant, be aware that clues can sometimes be misleading. For example, if  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  are both present, what color would you observe? Undoubtedly, the color depends on the proportions of each cation present.

### Chemicals

Known Solutions	Testing Solutions	Confirmation Solutions	River Samples
0.1 M $\text{AgNO}_3$	3 M $\text{HCl}$	0.2 M $\text{NaSCN}$	Computer Chips
0.2 M $\text{Cu(NO}_3)_2$	6 M $\text{NH}_3$		Paper Mill
0.2 M $\text{Fe(NO}_3)_3$	6 M $\text{NaOH}$		
0.2 M $\text{Zn(NO}_3)_2$	3 M $\text{H}_2\text{SO}_4$		
0.1 M $\text{Ba(NO}_3)_2$			

## Equipment & Materials

4 small, 4 large test tubes*	Parafilm squares	Plastic droppers	Centrifuge
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*\*Rinse and reuse the test tubes as needed.*

## Experimental Techniques

### Addition of Reagents

Always use a dropper when adding a small quantity of a liquid to a test tube. One mL is about 20 drops. If a reagent bottle has a dropper, replace it promptly after use. Do not allow the dropper to touch the container or solution to which you are adding the dropper's contents. Do not set the dropper down on the bench top or another surface, and be sure to return it to the right bottle. Always mix thoroughly after adding chemicals.

### Precipitation

To detect the formation of a precipitate on mixing two solutions, it is essential that both solutions be initially clear; if necessary, centrifuge to clarify. A "clear" solution is transparent but not necessarily colorless.

After adding a reagent to bring about precipitation, always test for complete precipitation if the purpose is to separate one substance from another. Suppose, for example, that a solution contains 0.10 millimole of  $\text{Ba}^{2+}$ . We add to this solution a few drops of dilute  $\text{H}_2\text{SO}_4$ , and the amount happens to contain 0.08 millimole of  $\text{SO}_4^{2-}$ . We have thus produced 0.08 millimole of solid  $\text{BaSO}_4$ , but 0.02 millimole of  $\text{Ba}^{2+}$  remains in the supernatant liquid, because we did not add enough  $\text{H}_2\text{SO}_4$  to precipitate all the  $\text{Ba}^{2+}$  as  $\text{BaSO}_4$ . This fact can be discovered by centrifuging and adding another drop of reagent (dilute  $\text{H}_2\text{SO}_4$  in this case) to the clear supernatant. If precipitation is complete, no additional precipitate will form. However, if insufficient reagent was added the first time, the additional drop will cause formation of more precipitate. If more precipitate is observed, add several more drops of reagent, centrifuge, and again test for completeness of precipitation. Repeat until no precipitate is formed on adding reagent. After the precipitate and supernatant are separated, the precipitate is washed by adding a few drops of the washing reagent (usually water), mixing thoroughly with a stirring rod, centrifuging, and removing the washings with a plastic dropper. Two or more washings are generally necessary to prevent contamination of the precipitate. **Failure to wash precipitates is one of the most common sources of error in qualitative analysis.**

### Heating of Solutions

To avoid excessive evaporation, use a water bath. Always stir when heating test tubes. A water bath with an aluminum test tube holder will be set up in the fume hood. Place test tubes into the water bath and heat the water to a gentle boil.

### Adjusting Acidity

Always stir well when adding acid or base. To test the pH of the solution, apply a drop onto litmus paper. Never dip the paper into the solution.

### Centrifuge

The centrifuge is used to speed up the separation of a precipitate from a liquid. When a mixture of solid and liquid is placed in a tube and rotated at high speed in a centrifuge, the precipitate is forced to the bottom of the tube by a centrifugal force that is many times greater than the force of gravity.

After centrifuging, the *supernatant*, or clear liquid above the precipitate, can easily be withdrawn with a plastic dropper.

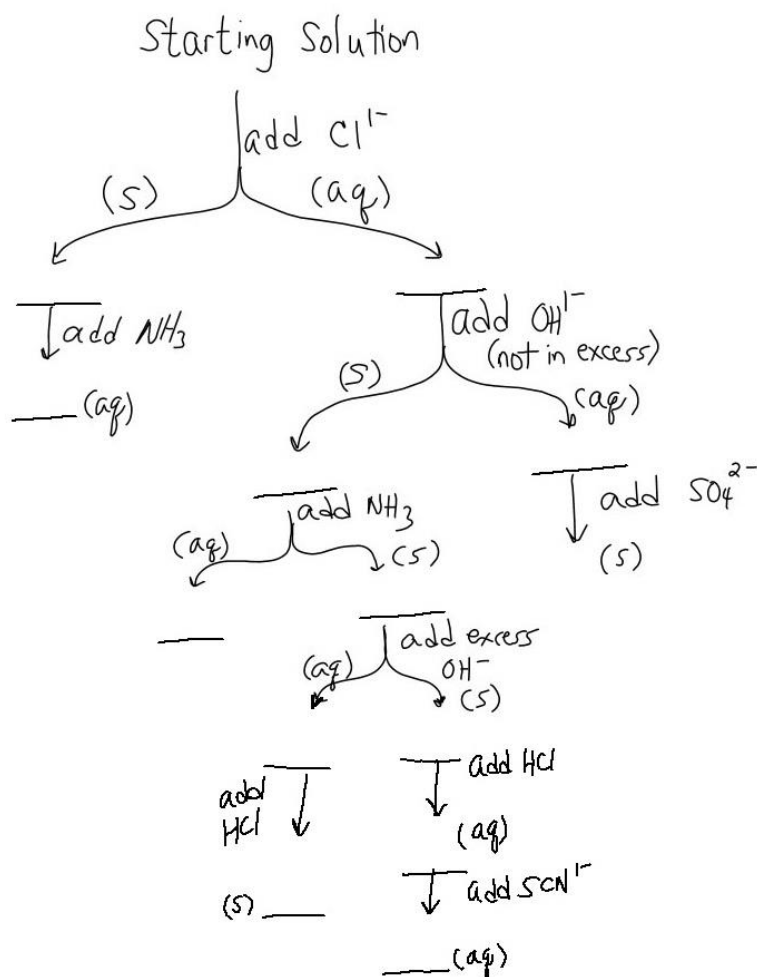
The centrifuge will be damaged if allowed to run unbalanced. Always insert an even number of test tubes in opposite positions in the centrifuge, noting their locations by number. The test tubes should contain approximately the same amount of liquid. Set the machine in motion for one minute, which should be sufficient to achieve effective separation of the solid from the liquid. Allow the centrifuge to stop spinning before trying to remove your test tubes.

### Experimental Procedure

#### Part A: Development of an Analysis Scheme

Use the information in the Qualitative Analysis Summary section above, along with the flow chart template in Figure 2 below, to map out an analysis scheme. This will give you a plan to follow for determining which ions are in your river samples. Draw this in your notebook and check your analysis scheme with your instructor before starting the lab work.

**Figure 2: Template for the Analysis Scheme**



**Part B: Separation Tests (Work with the known solution and both river water samples.)**

- 1) Use the dropper bottles of known solutions to put 10 drops of each cation into the same, one test tube. As you are doing this, record the color of each cation solution.
- 2) Obtain two different river samples, and put 50 to 60 drops of each sample into its own test tube.
- 3) Follow the analysis scheme as you perform the following tests on the solution of known cations and each river water sample. Record your observations for each step in your notebook.
- 4) Add 15 drops of 3 M HCl to the test tube containing the cations.
- 5) Centrifuge the test tube to separate the solid from the liquid. Separate and save the solid and the liquid for the next step.
- 6) Clean the solid from step 5.
- 7) Add 5 drops of 6 M NH<sub>3</sub> to the clean solid from step 6.
- 8) Add 1 drop of 6 M NaOH solution to the liquid from step 5. If no precipitate forms, add another drop of NaOH. If no precipitate forms, test the acidity of the solution with litmus paper. (Blue litmus turns red with acidic solutions; red litmus turns blue with basic solutions.) Add additional drops of NaOH solution if needed. You need a basic solution at this point, but not too basic. Mix well after each drop.
- 9) Centrifuge the test tube to separate the solid from the liquid. Save the solid and the liquid for the next steps.
- 10) Add 4 drops of 3 M H<sub>2</sub>SO<sub>4</sub> to the liquid from step 9. If a precipitate does not form, test the acidity of the solution with litmus paper. Add additional drops of H<sub>2</sub>SO<sub>4</sub> if necessary. You should see a precipitate form.
- 11) Clean the solid from step 9.
- 12) Add 5 drops of 6 M NH<sub>3</sub> solution to the clean solid from step 11. Test the basicity of the solution with litmus paper. You need a basic solution.
- 13) Centrifuge the test tube to separate the solid from the liquid. Save the solid for the next step.
- 14) Clean the solid from step 13.
- 15) Add 5 drops of 6 M NaOH solution to the clean solid from step 14.
- 16) Centrifuge the test tube to separate the solid from the liquid. Separate and save the solid and liquid for the next step.
- 17) Add 3 M HCl dropwise to the liquid from step 16. This is your confirmation test for Zn.
- 18) Observe the color of the solid from step 16. Add 3 M HCl dropwise until the solid dissolves.
- 19) Add 0.2 M NaSCN dropwise as a confirmation test for Fe<sup>3+</sup>.

**At this point, you should be at the bottom of the analysis scheme.**

Use your observations to determine the cations present in each of your river samples. Show your results to your instructor for feedback.

For the **Data section** of your notebook, make a table of tests performed, observations, and cations identified

For the **Results section** of your notebook, draw a completed analysis scheme with your observations and cation identifications.

For the **Conclusion section** of your notebook, comment on the accuracy of your results for the known sample and the two river samples.